



**Assessment of Some Chromated and Non-Chromated
Primers on Magnesium ZE41A, Aluminum 2024, and Steel
4340 Via Electro-chemical Impedance Spectroscopy**

by John V. Kelley

ARL-TR-3290

August 2004

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) August 2004		2. REPORT TYPE Final		3. DATES COVERED (From - To) January 2004 to May 2004	
4. TITLE AND SUBTITLE Assessment of Some Chromated and Non-Chromated Primers on Magnesium ZE41A, Aluminum 2024, and Steel 4340 Via Electro-chemical Impedance Spectroscopy			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) John V. Kelley (ARL)			5d. PROJECT NUMBER 622618-H80		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory Weapons and Materials Research Directorate Aberdeen Proving Ground, MD 21005-5069			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-3290		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Organic coating systems are one of the most efficient methods for protecting metals from corrosion, and the use of chromate primers vastly improves corrosion protection. However, environmental concerns about hexavalent chromium (Cr+6) toxicity have led to the development of many non-chromate coatings. In recent years, water-borne coatings have emerged as viable alternatives and provide the additional advantage of having low content of volatile organic compounds. Since the performance of chromated coatings tends to exceed that of their environmentally friendly counterparts, evaluations of some non-chromate alternatives need to be performed. This report compares the performance of three military primers: MIL-P-23377C (chromated), MIL-P-85582C (chromated), and MIL-P-85582N (non-chromated) on three common military alloys.					
15. SUBJECT TERMS chromated primers, coatings; magnesium corrosion; ZE41A					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 15	19a. NAME OF RESPONSIBLE PERSON John V. Kelley
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 410-306-0837

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1. Introduction

Organic coating systems have been one of the most efficient ways of protecting metal substrates from corrosion. The use of chromated primers in these systems vastly improves the corrosion protection. However, because of environmental concerns about hexavalent chromium (Cr+6) and because of stricter environmental regulations, many non-chromated coatings have been developed and are now being investigated for use on military systems. Water-borne epoxy coatings are being considered as a viable alternative to chromated coatings. A water-borne epoxy system comes with additional advantages such as lower content of volatile organic compounds, faster curing times, and easier cleaning, among others (*1*).

Although there are many environmental benefits for changing to the non-chromated primers, historically, the corrosion protection of these coatings tends to fall short of those containing chromate. Therefore, the goal of this study is to examine the performance of three military primers: MIL-P-23377C (chromated), MIL-P-85577C (chromated), and MIL-P-85577N (non-chromated) on three alloys that are commonly used in military systems: magnesium alloy ZE41A, aluminum alloy 2024-T3, and vacuum arc re-melted (VAR) 4340 steel. Specifically, electro-chemical impedance spectroscopy (EIS) was used to monitor and compare the corrosion behavior of the chromated versus non-chromated primers.

The three alloys in this study have very different corrosion behavior in chloride environments. The most sensitive is the magnesium alloy ZE41A. It has been reported that this alloy can corrode at a rate greater than 400 mils per year (mpy) (*2*). Magnesium alloys are typically used in the automotive industry in an effort to lighten automobiles, thus increasing gas mileage. The primary uses for magnesium alloys are for static structures such as supporting brackets and machine and transmission housings. Similarly, these alloys have found their way into some aerospace applications. Because magnesium alloys are lightweight and exhibit good strength and stiffness at room and elevated temperatures, a great deal of weight can be saved when magnesium transmission housings are used on rotary winged aircraft, which illustrates the importance of having a protective coating for magnesium alloys. The steel and aluminum alloys were chosen as representatives of typical materials used for many Army materiel structural components.

2. Experimental Procedure

2.1 Test Coupon/Panel Preparation (3)

Aluminum - Al2024-T3 samples were cleaned with an alkaline immersion tank cleaner (Turco 4215 or equivalent), deoxidized, and then rinsed with tap water followed by a flowing deionized water rinse. Panels were then immersion tank cleaned and mechanically scrubbed with a Scotch-Brite¹ pad (commercial item description [CID] A-A-58054, Type I Grade B or equivalent) followed with a water rinse just before the coating was applied.

Steel - 4340 panels were untreated (no cadmium plate) except that the surface was mechanically scrubbed with a Scotch-Brite pad (CID A-A-58054, Type I Grade B or equivalent) followed with a water rinse just before the coating was applied.

Magnesium - ZE41A-T5 alloy panels were cleaned by vapor degreasing or solvent wipe with military performance specification (MIL-PRF)-680 Type II or IV followed by acetone and were then mechanically scrubbed with a Scotch-Brite pad (CID A-A-58054, Type I Grade B or equivalent) followed with a water rinse just before the coating was applied.

All primers were applied in accordance with specifications MIL-P-23377 Type II Class C (control), MIL-PRF-85582 Type II Class C2, and MIL-PRF-85582 Type II Class N. Color-code 383 olive drab green was used for panel top coating. The recommended primer coating thickness per the cited specifications was 0.6 to 0.9 mil. Primer was applied as one full wet coat to the specified coating thickness.

2.2 Coating Thickness Measurements

The thickness of the coating on each of the samples tested was measured with an Elcometer² model 256FN eddy current thickness gauge. A total of five measurements was taken on each sample in the approximate locations shown in figure 1. The mean and standard deviations were recorded and are shown in table 1.

¹ Scotch-Brite™ is a trademark of the 3M Company.

² Elcometer® is a registered trademark of Elcometer, Inc.

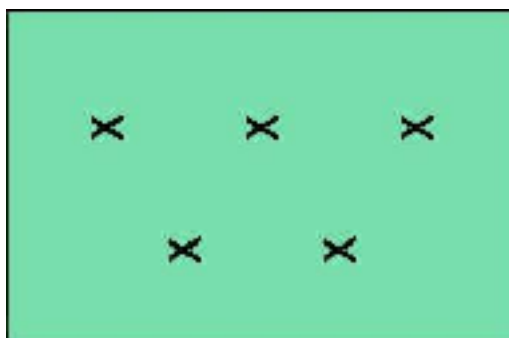


Figure 1. Schematic representation of a 3-inch by 5-inch test panel with an X indicating the approximate locations of each thickness measurement.

Table 1. Sample identification and thickness measurements.

Sample ID	Substrate Material	Primer (MIL-P-)	Mean Coating Thickness (mils)	Standard Deviation (mils)
33G4	Al 2024-T3	23377C	2	0.1
36G4	Al 2024-T3	85582C	1.3	0
39G1	Al 2024-T3	85582N	1.5	0
34G4	4340	23377C	2.77	0.17
37G4	4340	85582C	1.48	0.03
40G2	4340	85582N	1.69	0.07
35G2	ZE41A-T5	23377C	2.4	0.2
38G2	ZE41A-T5	85582C	1.8	0.4
41G2	ZE41A-T5	85582N	2.9	0.7

2.3 Electro-chemical Evaluation

EIS was employed to measure coating integrity over time. The apparatus used consisted of a Princeton Applied Research Model 283 potentiostat, a Schlumberger Model 1255 frequency response analyzer, and a Panasonic Model CF-71 laptop computer. The software package ZPlot³ was used for data acquisition and ZView⁴ for data analysis. Periodic measurements were taken at 2, 26, 46, 168, 480, and 672 hours of continuous immersion exposure with the cell configuration illustrated in figure 2. The cell was filled with 25 mL of 0.5 normal (N) sodium chloride (NaCl) solution and allowed to equilibrate for at least 2 hours before measurements were taken at the corrosion potential of the sample over the frequency range of 100 KHz to 0.01 Hz. The single sine technique was used, with an applied amplitude of 5 mV.

³ZPlot® is a registered trademark of Scribner Association.

⁴ZView™ is a trademark of Scribner Association.

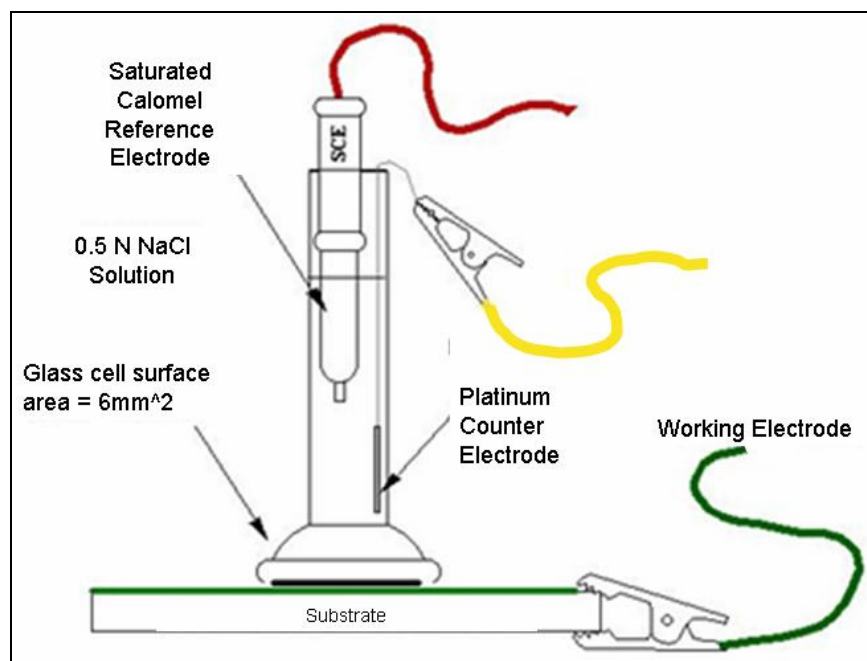


Figure 2. Electro-chemical corrosion cell configuration used for alternating current impedance measurements.

The maximum impedance at low frequency can distinguish between good and poor coatings (4). Therefore, the total impedance of the specimen, defined as the $\log |Z|$ value at 10 mHz in the Bode magnitude plot⁵, was plotted as a function of exposure time for comparison.

3. Results and Discussion

The mean coating thickness of each sample represented in the EIS data is presented in table 1. All the primer thicknesses are greater than the recommended thickness cited in the specification. Some were as much as 3 times the recommended thickness. The low standard deviation indicates that the coatings on each of the aluminum 2024 samples were the most consistent. It is also worth noting that the 4340 sample with primer 23377C was at least 63% thicker than either of the 85582 formulations on steel. Similarly, the 2024 sample with primer 23377C was more than 30% thicker than the other two primers on aluminum.

The surface condition of the ZE41A samples was much rougher than the other two alloys. Therefore, 10 measurements rather than 5 were taken on each sample in an attempt to gain more accurate measurements. However, there was no significant change in the standard deviation of these measurements.

⁵ A Bode plot is a standard way of graphically reporting electrochemical impedance values versus frequency.

3.1 Aluminum Alloy 2024-T3

The relative corrosion resistance of the aluminum alloy is evident in the EIS data presented in figure 3. As expected, the impedance value of the MIL-P-23377C primer remained in the 10^6 to 10^7 range. This supports the results of similar work previously reported by the U.S. Army Research Laboratory (5). The impedance values of the aluminum samples remain higher throughout the exposure period than those of either the steel or magnesium alloy. Although the performance of the 23377C chromated primer exceeded that of the other two primers on all alloys, the difference was not as significant in the case of the aluminum alloys as it was with the other substrates. After 46 hours of exposure, all three primers remained within an order of magnitude of each other, with the non-chromated 85582N exhibiting a slightly higher impedance value than the chromated 85582C.

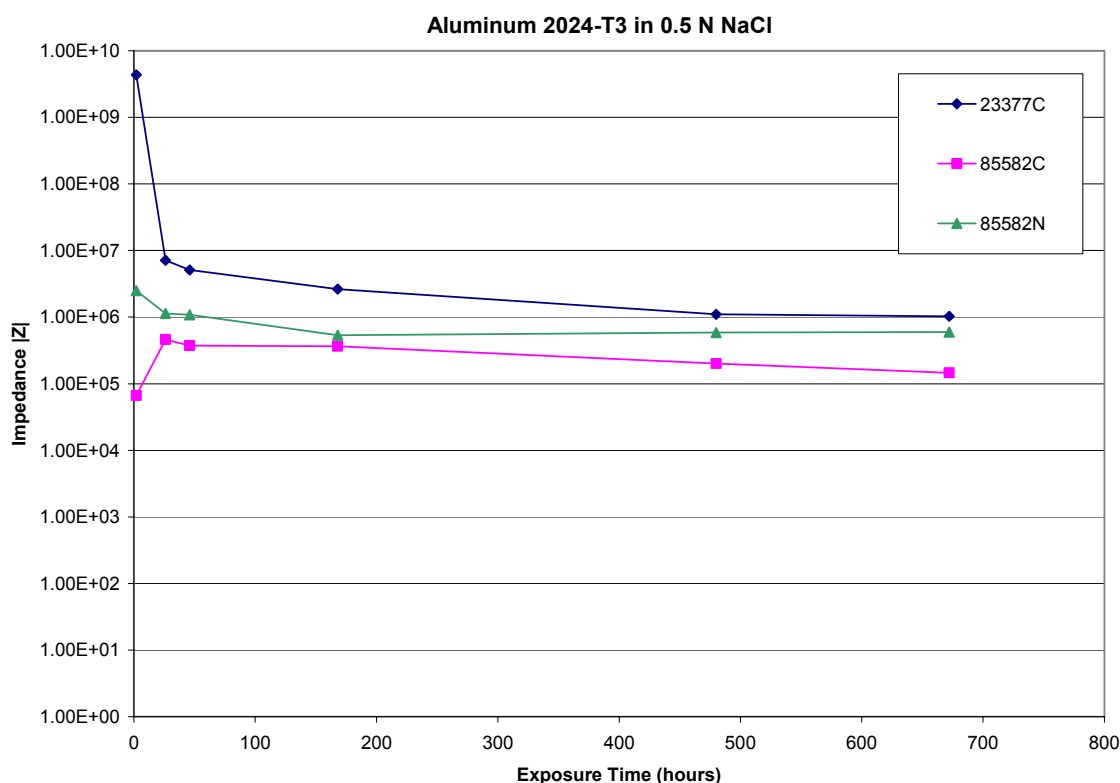


Figure 3. Low frequency impedance values versus exposure time in 0.5 N NaCl solution of primer-coated aluminum alloy 2024-T3.

3.2 4340 Steel

The performance of the 23377C chromated primer sample significantly exceeded that of both 85582C and 85582N on the steel samples, providing better corrosion protection as indicated by Z values that were several orders of magnitude higher. No red corrosion products were observed on this sample until the test was terminated and the cell removed. Conversely, corrosion was

soon evident on the other two primer samples. In the case of 85582C, blistering was observed at approximately 46 hours of exposure. This coincides with the drop in impedance at that point. While no blistering was noticed at this interval on the 85582N sample, the poor performance of both the chromated and non-chromated 85582 primers on steel (see figure 4) indicates that both coatings were compromised at this point. Their performances were nearly identical and there appears to be no benefit to using 85582C (chromated) instead of 85582N (non-chromated) on 4340 steel. It is also likely that the 23377C sample benefited from a coating 63% thicker than either the 85582C or 85582C primers.

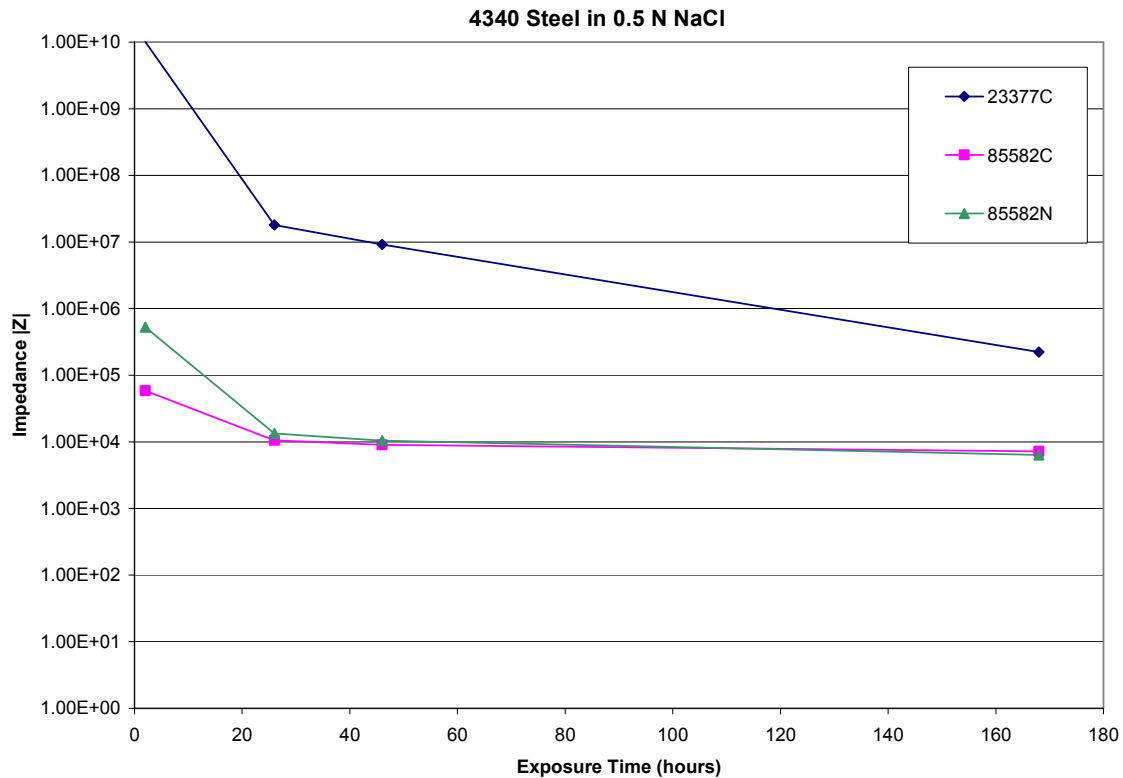


Figure 4. Low frequency impedance values versus exposure time in 0.5 N NaCl solution of primer-coated 4340 steel.

However, when the corroded surfaces in figure 5 are examined, a difference in the form of corrosion is clearly seen with the two 85582 primers. The chromated primer exhibited blisters that grew in number and size as exposure continued. The non-chromated primer appeared to erode somewhat uniformly before a blister was observed.

3.3 Magnesium Alloy ZE41A

It was anticipated that the primers on all the ZE41A magnesium alloy samples would perform inadequately for two reasons: first, historically, magnesium alloy ZE41A is very susceptible to corrosion. It has been reported that ZE41A corrodes at a rate greater than 400 mpy, making it

difficult to protect with only a primer. Secondly, because the ZE41A panels were sand casted, the surface roughness created some additional challenges. The roughness of some of the samples was so great that it was difficult to obtain accurate coating thickness measurements. Also, an extra effort had to be made in order for the corrosion cell (figure 2) to be successfully attached to the panel without leakage. Most importantly, however, the peaks and valleys of a rough as-cast surface lead to a nonuniform coating thickness. Coatings tend to be thinner and thus more vulnerable to corrosion initiation at the peaks. Since impedance is proportional to the coating thickness, the thinner regions at the peaks are reflected in the lower impedance measurements (see figure 6). The ZE41A panels with either 85582C or 85582N began actively corroding immediately upon exposure to the 0.5 N NaCl solution. The test was terminated after 3 hours for these two primers. Chang et al. (2) reports considerably different results for ZE41A using the same test parameters. Chang's samples were prepared with a 1-mil-thick coating system consisting of a Dow 17 pre-treatment and a Sermetel 1083 primer. These samples endured almost 100 days with an impedance value above 10^7 ohms-cm² while the best ZE41A sample in this experiment, primer 23377C, was at 10^5 ohms-cm², well below 10^7 . It maintained the highest impedance of the three primers tested on ZE41A, however. Although this is not meant to be a direct comparison, it may demonstrate the importance of using a good pretreatment on magnesium alloys.

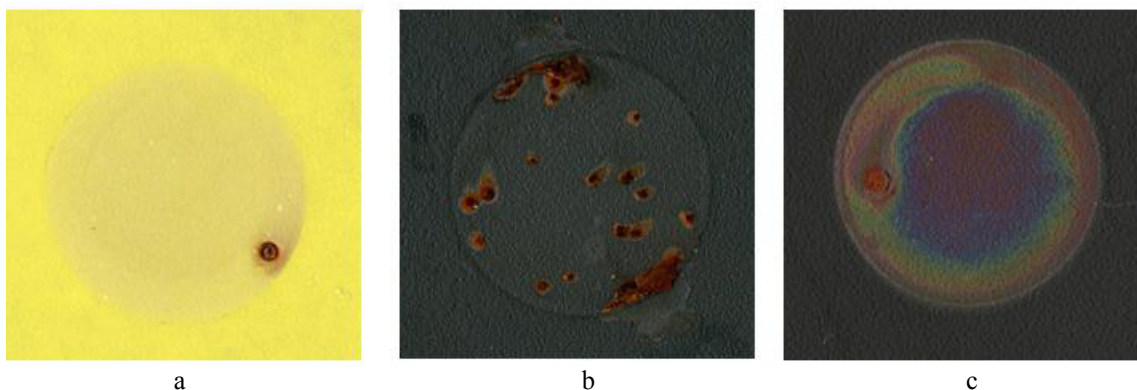


Figure 5. Area under corrosion cell of 4340 after 53 days of exposure: a) chromated primer 23377C, b) chromated primer 85582C, c) non-chromated primer 85582N.

Exposure to the 0.5 N NaCl solution was allowed to continue to 53 days. Figure 7 shows the significant damage sustained by all the ZE41A samples. The yellow arrow in the middle photograph points to a spot where a hole was created when the ZE41A corroded through to the back side, which caused solution to leak out of the cell. It can be seen in figure 7c that there was considerable corrosion around the perimeter, which caused leakage underneath the o-ring.

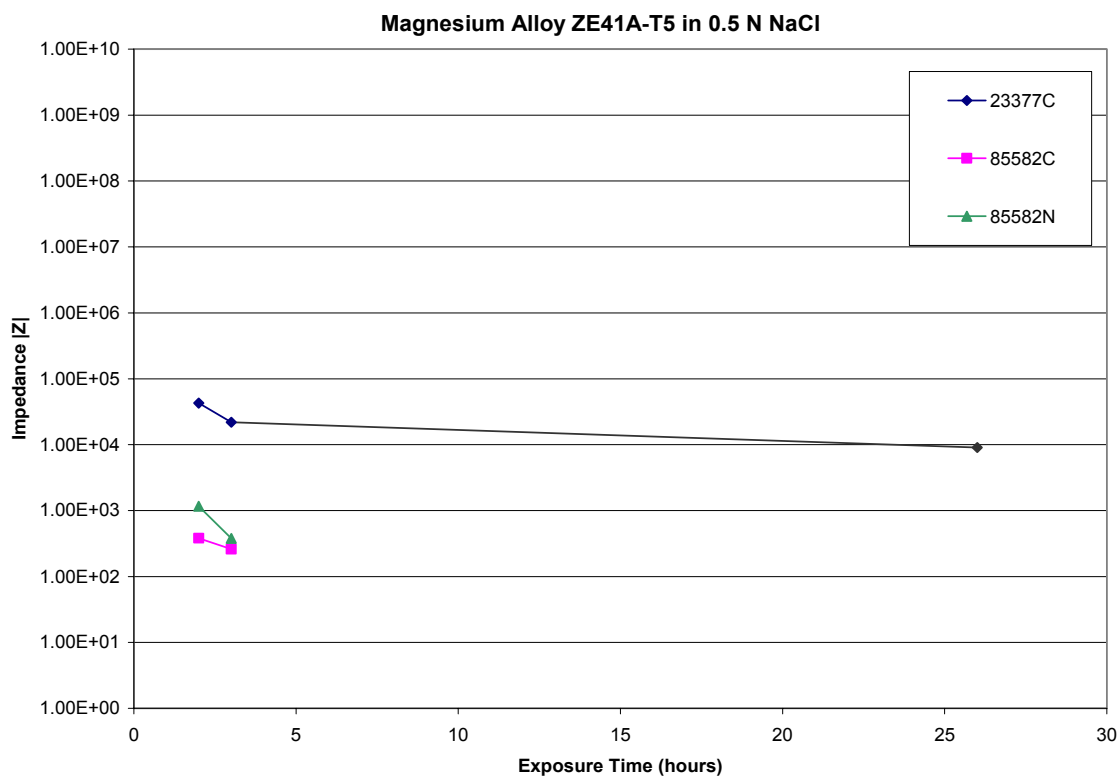


Figure 6. Low frequency impedance values versus exposure time in 0.5 N NaCl solution of primer-coated ZE41A-T5 magnesium alloy.

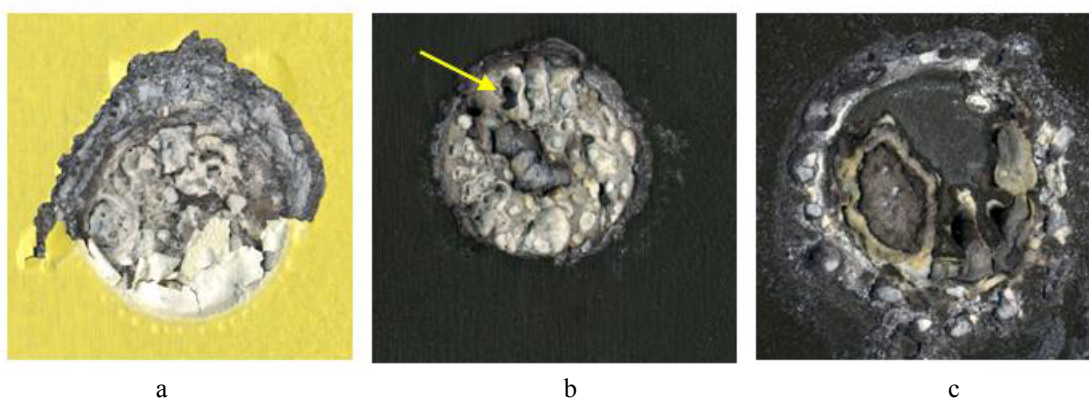


Figure 7. Area under corrosion cell of ZE41A after 53 days of exposure: a) chromated primer 23377C, b) chromated primer 85582C, c) non-chromated primer 85582N.

4. Conclusions

1. MIL-P-23377C provided the best initial corrosion protection across all three alloys tested. However, all primers on Al 2024 provided similar protection beyond 46 hours of immersion in 0.5 N NaCl.

2. Neither of the MIL-P-85582 primer formulations proved to be an effective alternative to MIL-P-23377C on either the VAR 4340 steel or the ZE41A magnesium.

3. Because the ZE41A magnesium was tested without a pre-treatment, the 0.5 N NaCl solution proved to be too aggressive, and all the coatings failed prematurely, illustrating the value of pre-treatments on magnesium alloys.

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